A type of ecocement prepared from municipal solid waste incineration fly ash

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ABSTRACT: This paper presents the laboratory scale study on the preparation of alinite ecocement clinkers from municipal solid waste incineration (MSWI) fly ash. Firing schedule, microscopy, compressive strength of the clinker was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), etc. The ratio of some heavy metals volatilized during clinkerization, as well as leaching concentration of free Cl\textsuperscript{−} in the ecocement were also investigated. From the results it is observed that alinite ecocement can be prepared from MSWI fly ash under the temperature of 1200°C and duration time of 1h. The addition of 20% MSWI fly ash as admixture in alinite ecocement reduces the early day strength significantly, but exerts little influence on compressive strength at later ages. Results also show that most of Cl\textsuperscript{−} in the ecocement pastes existing in condition of bounded with clinker mineral or hydration products, but the amount of leaching free Cl\textsuperscript{−} was significant, and the steel bar exposed to the alinite ecocement is likely to be corroded.

1 INTRODUCTION

Ecocement is a new type of cement produced with recycled materials. The present research mainly involves the preparation of alinite cement from wastes such as municipal solid waste incineration (MSWI) ash (Chang et al., 2005). Alinite has a crystal structure similar to alite (C\textsubscript{3}S) in which oxygen ions are partially substituted by chlorine and silica by alumina, and it can be represented by the general formula: Ca\textsubscript{10}Mg\textsubscript{1−x/2}V\textsubscript{x/2}[(SiO\textsubscript{4})\textsubscript{3−x}(AlO\textsubscript{4})\textsubscript{x}]O\textsubscript{2}Cl (V: a lattice vacancy; 0.35<x<0.45) (Ilyukhin et al., 1977; Lampe et al., 1986; Neubauer et al., 1994; Pradip et al., 1990). Alinite has characteristics of a low clinkering temperature, comparable or even superior hydraulic properties, and easy grindability when compared to Ordinary Portland Cement. The hydration products of alinite have a capability to fix heavy metals in the crystal lattice, which can be used to immobilize hazardous waste materials (Chang et al., 2005; Kim et al., 2003; Singh et al., 2008).

Treatment of municipal solid waste (MSW) by incineration has been widely used in China due
to its many advantages, such as mass and volume reduction disinfection, reduction of organic matter and so on (Wang et al., 2010). It is estimated that there are about 75 MSWI plants in China and the total capacity has reached 33 thousand tons per day. Nevertheless, MSWI produces a large amount of fly ash up to the proportion of 3-5 wt% of the original waste amount. Due to the presence of leachable high concentrations of heavy metals and soluble salts which are caused by transfer of volatile species to the off-gases in the combustion chamber and subsequent condensation of such species in the air pollution control units, and residual amounts of hazardous organics (e.g., dioxins), MSWI fly ash is classified as a hazardous matter in many countries and must be treated prior to disposal to avoid damaging the environment (Fuoco et al., 2005; Ferreira et al., 2005; Wan et al., 2006; Park et al., 2009; Qian et al., 2009).

The recycling of industrial waste in civil engineering applications has undergone considerable development over a very long time. Coal fly ash, blast furnace slag and silica fumes are examples of the success of this research. Recently, several researches have studied the possibility of recycling MSWI fly ash in the cement and concrete manufacturing, especially as raw materials for production of Portland cement clinker (Lin et al., 2005; Pan et al., 2008; Singhal et al., 2008). Although several advantages of preparing Portland cement from MSWI fly ash have been described (e.g. improving the burnability of the raw mix and reducing heavy metal leachability based on the hydration products) in previous studies (Aubert et al., 2006; Canpolat et al., 2004; Lin et al., 2003; Wang et al., 2001), certain problems cannot be ignored: (1) production of Portland cement requires a large amount of calcium-rich raw materials (the lime contents for major clinker minerals $C_3S$, $C_2S$, $C_3A$ and $C_4AF$ are 73.7%, 65.1%, 62.2% and 46.2%, respectively), and therefore it would not be able to utilize MSWI fly ash in large quantities; (2) Portland cement is very sensitive to the presence of impurities in MSWI fly ash and the utilization of MSWI fly ash for Portland cement production is restricted as a result.

In order to reuse of MSWI fly ash in large quantities and low energy consumption, the utilization of it in chlorine bearing alinite ecocement production was proposed in some reports (Singh et al., 2008; Vaidyanathan et al., 1990). In this paper, the feasibility of reusing the MSWI fly ash as raw materials in alinite ecocement was evaluated. The sintering temperature in the furnace could be selected under the temperature of 1200 $^\circ$C which is about 200 $^\circ$C lower than that of Portland cement. The cement quality was investigated to evaluate the reuse feasibility of MSWI fly ash in ecocement production.

## EXPERIMENTAL

### 2.1 Raw materials and preparation

MSWI fly ash used in this investigation was collected from Suzhou Wastes Incineration Plant in China. The chemical compositions of MSWI fly ash is given in Table 1. Reagent grade chemicals, $CaCO_3$, $CaCl_2$, $CaSO_4\cdot2H_2O$, $SiO_2$, $MgO$ and $Al_2O_3$, were also used to adjust the compositional parameters. All the materials were ground and sieved through a 200-mesh sieve.

| Table 1. Chemical composition of raw materials (by wt.%) |
|---|---|---|---|---|---|---|---|---|
| MSWI FA | CaO | SiO$_2$ | CaCl$_2$ | SO$_3$ | Al$_2$O$_3$ | K$_2$O | Na$_2$O | Fe$_2$O$_3$ | MgO | LOI |
| 29.8 | 13.9 | 10.8 | 6.8 | 3.7 | 3.5 | 3.2 | 1.5 | 1.5 | 25.2 |
2.2 Experimental methods

All the raw materials were blended in proportions following the Cement Modulus (Eqs.(1)-(3)): Lime saturation modulus ($KH=1.0$), Silica-alumina ratio ($a=4.5$), Silica-chloride ratio ($c=2$) and MgO content ($m=1.40$). The replacement of MSWI fly ash was 30% as raw material.

$$KH = \frac{CaO\,(wt.\%)}{2.608SiO_2\,(wt.\%)} - 0.7Fe_2O_3\,(wt.\%)$$ (1)

$$a = \frac{SiO_2\,(wt.\%)}{Al_2O_3\,(wt.\%)}$$ (2)

$$c = \frac{SiO_2\,(wt.\%)}{CaCl_2\,(wt.\%)}$$ (3)

$$m = MgO\,(wt.\%)$$ (4)

All the raw materials in predetermined proportions were weighted accurately (30g) and then mixed in isopropyl alcohol thoroughly. The resultant mixture was dried in an oven at 65 °C for 1 day, then pressed and moulded into cylindrical samples of $\Phi 30 \times 5 \text{ mm}^3$. The cylinders were fired in furnace at different temperature and an average heating rate of about 30 °C/min was employed. After the firing, the samples was removed from the furnace and cooled at ambient temperature rapidly.

The phase of the clinker was determined by X-ray diffraction (XRD). The morphology of the clinker was performed by scanning electron microscopy (SEM). The heavy metals concentration in the clinker was determined by inductively coupled plasma atomic emission spectrophotometer (ICP-AES).

The selected clinker with MSWI fly ash and gypsum as cement admixture was ground to making alinite ecocement. The cement samples were mixed with water with the W/C ratio of 0.3 and the paste was put into the $10 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$ cube moulds with vibration. The molded pastes were kept at 20±2 °C and relative humidity exceeding 90% for 24h, and then removed from the molds. The demoulded samples were cured in a water tank at 20±2 °C for 1, 3, 7 and 28 days and then tested for compressive strength.

The chloride present in the raw mix improves the burnability of the raw mix and promotes the formation of alinite and $C_2S$ phases at low temperature with subsequent reduction in f-CaO. While most of the chloride is lost due to volatilization on firing, some is still retained in the cement in a fixed form (2-3 wt.%) and a small amount (about 1%) as free chloride (Singh et al., 2008) that is responsible for the corrosion of steel bar in concrete. To assess this potential impact, leaching test was performed and the free Cl$^-$ content was measured by the volumetric solution of AgNO$_3$. The test method of leaching Cl$^-$ was prepared according to Chinese Ministry of Transport Standard JTJ 270-98 (testing code of concrete for port and waterwog engineering).
3 RESULTS AND DISCUSSION

3.1 XRD analysis of the clinker

The firing temperatures were selected at 1050°C, 1100°C and 1200°C, while the duration time was selected to be 1h, 2h and 4h. The XRD patterns of alinite clinkers fired in different temperatures and different duration time were shown as Figure 1 and Figure 2.

Figure 1. XRD patterns of alinite clinkers fired at different temperature for 1h.
Figure 2. XRD patterns of clinkers fired at 1200°C for different duration time.
Figure 1 (a) shows that the formation of $C_{11}A_7\cdot CaCl_2$ is not dependent upon the temperature in range of $1050 ^\circ C$~$1200 ^\circ C$. The effect of firing temperature is noticed in the relative proportion of alinite and $\beta$-C$_2$S. The formation of alinite increases with increase in the firing temperature (from $1050 ^\circ C$ to $1200 ^\circ C$), with a corresponding decrease in the formation of $\beta$-C$_2$S. In the case of the alinite peak ($d=3.23\AA$), the intensity of the peak was increased from 1766 to 3900 after increasing the firing temperature from 1050$^\circ C$ to 1200$^\circ C$ (Figure 1 (b)).

As shown in Figure 2, with increase in firing time, there was (a) a slight increase in the formation of alinite; (b) no effect on other phases; and (c) all the reactions seem to be over within 1 h. Considering the composite of phase and energy consumption, it is concluded that the good quality clinker can be obtained on firing the raw mix at 1200 $^\circ C$ for 1 h.

3.2 SEM analysis of the clinker

The SEM photos of alinite clinker fired at 1200 $^\circ C$ for 1 h are shown in Figure 3. The clinker was high porous (Figure 3 a), irregular (Figure 3 c) and plate-like (Figure 3 d). Figure 3 b was the resultant of liquid phase reaction.

Figure 3. SEM photos of alinite clinkers.

3.3 Compressive strength of the ecocement

Four kinds of alinite ecocement were prepared by grinding the clinkers with gypsum and MSWI fly ash to a fineness of 400m$^2$/kg (Blaine). The compressive strength of cements in different curing ages was tested. The results were illustrated in Figure 4. As displayed in Figure 4, sample A has the highest compressive strength in all curing ages. The 1 day compressive strength of all samples increases in the following sequence A>B>C>D, but the compressive strength of sample D develops faster than that of B and C between 1 day and 28 day. The results indicate that the
addition of 20% MSWI fly ash as admixture in alinite ecocement reduces the early day strength significantly, but exerts little influence on compressive strength at later ages.

Figure 4. Compressive strength of alinite ecocement samples. (A) 95% clinker with 5% gypsum; (B) 90% clinker with 5% gypsum and 5% MSWI FA; (C) 85% clinker with 5% gypsum and 10% MSWI FA; (D) 75% clinker with 5% gypsum and 20% MSWI FA.
3.4  Behaviour of heavy metals

The determined heavy metals concentration in the MSWI fly ash samples and the alinite clinkers were measured as shown in Figure 5. It is shown that more than 85% Cd, Zn and Pb are volatilized during the clinkerization. However, over 70% of the Ni, Cr and Cu are fixed in the clinker. Heavy metals like Cd, Zn and Pb might be present as CdCl₂, ZnCl₂ and PbCl₂ due to high amounts of chloride in the MSWI fly ash. These compounds would be volatilized at high temperature during the clinkerization process because of their relatively low boiling point (the boiling points of CdCl₂, ZnCl₂ and PbCl₂ are 960, 732 and 950 °C, respectively) (Saikia et al., 2007). Heavy metals like Ni, Cr and Cu are not volatilized during the clinkerization could be due to these metals reacted with other constituents and form some stable compounds.

![Figure 5. Behaviour of some heavy metals during the clinkerization](image)

3.5  Free Cl⁻ leaching test

The free Cl⁻ concentration of the fired ecocement in different curing ages is shown in Figure 6. The free Cl⁻ concentration was in the range of 0.210-0.153% at different curing ages, which implied that most Cl⁻ in the ecocement pastes existing in condition of bounded with clinker minerals or hydration products. As curing age increases, the free Cl⁻ concentration decreased gradually for part of free Cl⁻ is bounded in the new hydrates, and it attains to a steady-state after 14 days of hydration. Additionally, the free Cl⁻ content in the cement pastes is higher than the limit permitted (0.06%) in Chinese National Standard GB/T 50010-2002 (Code for design of concrete structures). Therefore, the steel bar exposed to the alinite eco-cement is likely to be corroded.
Figure 6. Free $\text{Cl}^-$ concentration of sample A3 in different curing ages.
4  CONCLUSIONS

The possibility of reusing MSWI fly ash in large quantity as a major cement raw material in alinite ecocement production has been demonstrated in this report. From the XRD patterns and energy consumption, it can be concluded that the best results were obtained on firing the raw mix at 1200 °C for 1h.

The alinite clinker appeared as irregular and plate-like particles. During the clinkerization process, different heavy metals exhibit different volatilization behaviour. Additionally, the release of free Cl\(^-\) was significant during hydration, and the steel bar exposed to the ecocement is likely to be corroded.

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6  REFERENCES


